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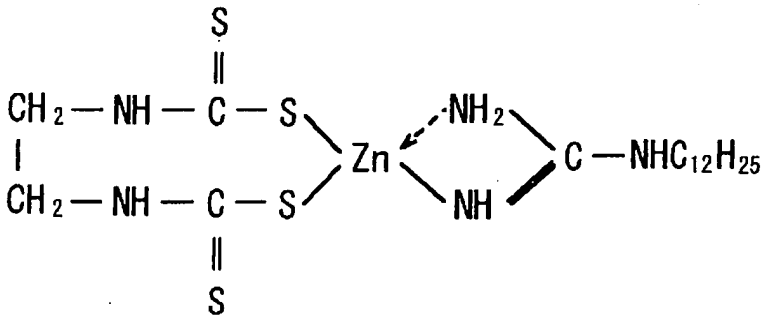
Agricultural Fungicides

Brief Description of a Drawing

Fig. 1 shows an infrared absorption spectrum of the double salt of zinc ethylene bisdithiocarbamate and n-dodecylguanidine.

Detailed Description of the Invention

The present invention relates to agricultural fungicides containing as an effective component the double salt of zinc ethylene bisdithiocarbamate and n-dodecylguanidine, represented by the formula:



At present, n-dodecylguanidine acetate has mainly been used as chemicals for disease control in fruit trees. It has

frequently been recognized, however, that since n-dodecylguanidine acetate is a dissociating salt, it disadvantageously may give a chemical injury to plants or alter other chemicals that have been added to fungicides or insecticides for the purpose of expansion of the effect.

The present inventors made a series of studies to eliminate such disadvantages of the above-mentioned chemicals. They finally found that the double salt formed with n-dodecylguanidine and zinc ethylene bisdithiocarbamate exhibits a potent fungicidal effect but it has no chemical injury or adverse effect to other mixed chemicals, which adverse effect was observed in the use of n-dodecylguanidine acetate. Thus, the invention was completed.

The novel compound as an effective component in the invention may easily be prepared as yellowish white crystals very sparingly soluble in water or organic solvents by making zinc chloride or zinc sulfate act on a mixed solution of sodium (or ammonium) ethylene bisdithiocarbamate and n-dodecylguanidine. Said crystals decompose at 200°C or higher and exhibit an infrared absorption spectrum as shown in Fig. 1.

The agricultural fungicides of the invention can be used in disease control of a variety of field crops such as apple leaf spot defoliant disease, pear black spot disease, and the like.

The following experiments demonstrate the excellent preventive effect of the compound as effective component of the invention.

Experiment 1

Control test for apple leaf spot defoliant disease by a green leaf method

The green leaves of apple (Star King Delicious) collected by cutting were immersed in a chemical solution diluted in a pre-determined concentration. The leaves were removed from the solution, dried, and inoculated with spraying of the microbe of apple leaf spot defoliant disease. After keeping at a moist temperature of 27°C for 3 days, development of disease spots was observed. Table 1 shows the results.

Table 1

Chemical tested		Development of Disease Spots (Concentration mcg/ml)		
		1000	500	250
Compound of Invention		1	1	2
Compound	Difoltan	1	2	2
No Application	Microbe		5	
	NO microbe		0	

Note 1: Development of disease spots was represented by the following 6 degrees according to the rate of infected area.

Wholesome 0

Infected area 1 - 20% 1

" 21 - 40% 2

" 41 - 60% 3

" 61 - 80% 4

" 81 - 100% 5

Note 2: Difoltan (trade name): N-Tetrachloroethyl-4-cyclohexene-1,2-dicarboxyimide

As seen from Table 1, the agricultural fungicide of the invention showed a markedly preventive effect on an apple leaf spot defoliant disease.

Experiment 2

Pot test for preventive effect on a pear black spot disease

To the saplings of pear (twenty century species) was sprayed a chemical solution at a rate of 100 ml per tree. After drying, the spores of pear black spot disease microbe was inoculated and kept overnight in a moist room. After standing in a green house for 4 days, the degree of development of lesions was observed. Table 2 shows the results.

Table 2

Chemicals Tested		Concentration (ppm)	Incidence of disease	Index of Effect
Compound of Invention	20% Wettable powder	1000	51.6	83.4
Control Compound	Difoltan 80% Wettable powder	1000	72.0	80.4
No application		-	100.0	0

Note 1: The index of effect in Table 2 was calculated as follows.

Index of effect = [1-(morbidity index A in the sprayed area/ morbidity index A in the area of no application)] x 100

wherein A= [(ax0)+(bx1)+(cx2)+(dx3)]/(a+b+c+d)

a: Number of wholesome leaves

b: Number of slightly infected leaves (infected 1/3 or less of the leaf are)

c: Number of moderately infected leaves (infected 1/3 to 2/3 of the leaf are)

d: Number of severely infected leaves (infected 2/3 or more of the leaf are)

Note 2: Difoltan: the same as in Note 2 of Table 1.

As seen from Table 2, the agricultural fungicide of the invention showed a markedly preventive effect on a pear black spot disease.

Experiment 3

Preventive effect on a pear black spot disease (field test)

To the 4-year old saplings of pear (twenty century species) was sprayed a chemical solution at a rate of 1 L per tree 8 times at intervals of 14 days. One week after the final spraying, occurrence of a pear black spot disease was observed.

Table 3 shows the results.

Table 3

Chemicals Tested		Concentration (ppm)	Incidence of disease	Chemical injury
Compound of Invention	20% Wettable powder	1000	51.6	none
Control: n-Dodecylguanidine acetate	65% Wettable powder	1000	80.9	yes
Control: Zinc ethylene bis-dithicabamate	65% Wettable powder	1000	70.2	none
No treatment			100	—

As seen from Table 3, the agricultural fungicide of the invention showed a markedly excellent preventive effect on a pear black spot disease with less chemical injury in comparison with n-dodecylguanidine acetate or zinc ethylene bisdithiocabamate.

Experiment 4

Chemical Injury Test

To the saplings of pear (Chojuro species) was sprayed a chemical solution at a rate of 100 ml per tree 5 times at intervals of 13 days. The occurrence of chemical injury was observed 10 days after the final spraying. Table 4 shows the results.

Table 4

Chemicals Tested		Concentration (ppm)	Incidence of Injury (%)	Degree of Injury Occurrence
Compound of Invention	20% Wettable powder	4000	12.7	0.14
		2000	4.6	0.07
		1000	0.2	0.01
Control: n-Dodecylguanidine acetate	65% Wettable powder	4000	21.0	0.40
		2000	15.2	0.16
		1000	6.5	0.04
Area of no treatment		—	0	0

Note: Incidence of chemical injury and the degree of injury occurrence were calculated as follows.

Incidence of Chemical Injury = [(Number of saplings injured)/(Total number of saplings)] x 100

Degree of Occurrence = (Ax3+Bx2+Cx1)/Total leaf number

In the above formulae,

A: Number of leaves on which 2/3 or more area is injured with spots.

B: Number of leaves on which 2/3 - 1/3 of area is injured by spots.

C: Number of leaves on which 1/3 or less area is injured by spots.

From the above table, it is recognized that the injury due to the agricultural chemical of the invention is greatly reduced in comparison with n-dodecylguanidine acetate.

When the compound as an effective component of the invention is used as an agricultural fungicide, it may be formulated together with a proper carrier and used in a form

such as wettable powder, dust, granules, tablets, or if required as an emulsion. The above carrier means a material delivering the compound for contact with pathogens, or filler. The solid carrier includes clay, kaolin, talc, diatom earth, silica, and calcium carbonate. The liquid carrier includes benzene, alcohol, acetone, xylene, methylnaphthalene, cyclo-hexanone, dimethylformamide, dimethylsulfoxide, animal or plant oil, fatty acids, their esters, and various surface activating agents.

Auxiliary chemicals conventionally used in agricultural chemicals, for example, spreader, emulsifying agent, wettable agent, and sticking agent, may properly be admixed to make sure the effect.

The compound as an effective component or agricultural compositions of the invention may be used as a mixture with other agricultural fungicides, insecticides, nematicides, herbicides, plant growth regulators, soil conditioners, or fertilizers.

The invention will specifically be illustrated by the following examples.

In these examples, "part" indicates "part by weight".

Example 1

The effective compound (20 parts) is mixed with 80 parts of excipient such as clay to give wettable powder. This preparation is suspended in water to use as a spraying solution.

Example 2

The effective compound (5 parts) is mixed with 60 parts of talc, 30 parts of bentonite, and 5 parts of dispersant and wetting agents, and the mixture is crushed to give dust. In using this preparation may be sprayed directly.

CLAIM

1. An agricultural fungicide containing as an effective component the double salt of zinc ethylene bis-dithiocarbamate and n-dodecylguanidine, represented by the formula:

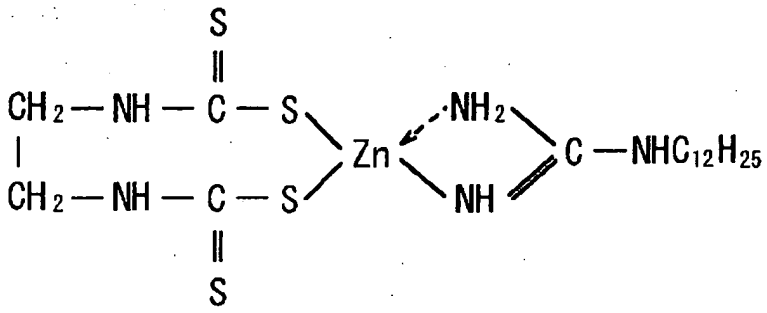


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FIG. 1